

Removal of sulphates from aluminium powder coating effluent using basic oxygen furnace slag and granulated blast furnace slag

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Abstract. Pollution of South Africa water puts a strain on natural resources and Aluminium Powder Coating Effluent (APCE) is one of the pollution sources among industrial effluents. These effluents contain high levels of sulphates about 1230 ppm. This study only focused on the removal of sulphates. The objective of this study was to investigate the removal of sulphates from APCE using Basic Oxygen Furnace Slag (BOFS) and Granulated Blast Furnace Slag (GBFS) as an adsorbent. BOFS was used as the basis of all the experiments as it increased the pH of the effluent to be around 12. BOFS removed more than 80% of sulphates. Adsorption experiments were carried out under different operating conditions. Freundlich and Langmuir isotherms were studied and the experimental data best fitted the Langmuir model. Adsorption kinetics was also studied and the pseudo second order gave the best fit at all operating conditions. This brought about a conclusion that BOFS can be used as an adsorbent for removal of sulphates.

1. Introduction

Sulphates in water have been a big problem for industrial plants that discharge their effluent to the municipal because they have to ensure that the level of sulphates are low. However, water resources in South Africa are limited and are declining as the population grows and consumption increases. Thus, stricter water quality regulations and discharge standards are being imposed to allow for its re-use or its safe disposal into the environment [1]. The removal of sulphates helps in protecting the health of humans, domestic animals, and the fauna and flora in the environment. Sulphates are not toxic to humans except very high concentrations above 400 mg/L, maximum contamination level in South Africa [2]. However, they do increase total dissolved solids (TDS), salinity, impart taste and odour to drinking water at lower concentrations. This can cause digestive disorders at concentrations that are typically found downstream of mining and other industrial operations. For domestic and wild animals, drinking water containing sulphates can cause similar ailments and possible reproductive disorders [3].

It is therefore important to encourage industries to minimize water consumption, and recycle and re-use water and effluent where possible. Industrial effluents produced in South Africa namely textile and powder coating effluents are considered problematic. These effluents especially in terms of colour, chemical oxygen demand (COD), salinity, TDS, toxic metals and most importantly sulphates [3-4].

Aluminium powder coating effluent (APCE) is waste water from the pre-treatment process where aluminium is pre-treated before painting to reduce the chances of aluminium corroding. Tap water is used in this pre-treatment process for rinsing the aluminium, sulphuric acid and water are used in the



pickling bath. Then aluminium goes through the chrome and water bath where chrome is used to create a protective layer which increases adhesion between the aluminium and the paint. APCE consists of water from the pickling bath where water is mixed with sulphuric acid and water from the settling tanks where hexavalent chromium (Cr^{6+}) is reduced to trivalent chromium (Cr^{3+}) by using sodium metabisulphite. Hexavalent chromium (Cr^{6+}) is hazardous to both environment and humans as it can cause cancer and other medical conditions. Hence it is advisable to reduce it to trivalent chromium (Cr^{3+}) which is a trace element for humans and animals. The use of sodium metabisulphite is an easy process for reducing chromium [5].

Most of the metals can be easily removed by chemical precipitation. However, due to the high solubility of sulphates they are more difficult to remove by chemical precipitation [5]. Thus, adsorption as an alternative to sulphate removal was considered in this study due to its low cost, ease of operation and effectiveness [6]. Basic Oxygen Furnace Slag (BOFS) was chosen as adsorbent for this study due to its low cost. As it is by-product of the steel manufacturing process and are readily available in South Africa. This will add information on previous uses of BOFS as adsorbent.

The Basic Oxygen Furnace slag (BOFS) or Blast furnace sludge is a great adsorbent for metal and sulphates removal from aqueous solutions [7]. BOFS has been used for the removal of phosphorus from wastewater and an average of 86% was recovered [8]. The following results were observed and reported on the use of BOFS for P exclusion from wastewaters, it was resolved that slag materials eradicate P to different forms dependent on laboratory conditions [9].

2. Materials and methods

APCE was collected from Wispeco Aluminium powder coating pre-treatment effluent plant. BOFS and GBFS were used as adsorbents and were supplied by ArcelorMittal (South Africa). Analytical grade hydrochloric acid (Sigma Aldrich) and sodium hydroxide (Rochelle Chemicals) were used to adjust the pH of the effluent.

2.1. Equipment

Adsorption experiments were conducted in a thermostatic shaker (Labotec OrbiShaker). XRD (Ultima IV Rigaku) equipped with a copper target was used to determine the mineralogical composition of the slag before and after adsorption. A UV Visible Hach spectrophotometer (DR3900) was used to measure sulphate content. A pH meter was used to measure the pH level of APE. Vacuum filtration was used to filter the mixture of waste water and slag after adsorption prior to sulphate analysis.

2.2. Methodology

Initially screening tests were conducted to determine the most effective adsorbent between BOFS and GBFS. Thereafter, based on the results obtained further adsorption studies were conducted using BOFS to determine the effect of solid loading, residence time and temperature.

2.2.1. Adsorbent dosage (solid loading) Different masses of BOFS (2-10 g) were placed in 6 conical flasks and 100 ml of APCE was added to each flask and was agitated for 1 hour in a thermostatic shaker maintained at 25°C. After agitation the samples were filtered using a Buchner funnel and the filtrate was analysed for sulphates. The solid loading giving the highest sulphate removal was used in the subsequent experiments to determine the effect of residence time and temperature.

2.2.2. Effect of residence time and temperature 100 ml of APCE was mixed with a pre-determined mass of BOFS and 4 mixtures were prepared. The 4 mixtures were agitated at different time intervals respectively in a thermostatic shaker at 200 rpm and 25°C. After each time interval agitation was stopped and the solutions were subsequently filtered using a Buchner funnel and the filtrate was analysed for sulphate.

The above procedure was repeated at 35°C and 45°C to study the effect of temperature on sulphate removal.

2.2.3. Sulphate and XRD analysis APCE samples before and after adsorption were filtered and 25 ml aliquot of the APCE was transferred into 25 ml sample cell. A quarter of a spoon of barium chloride was added to the sample cell and the cell was swirled to dissolve the powder. The content of the cell was then allowed to react for 5 min before colorimetric measurement. The reaction of barium with the sulphate ions present in the sample results in insoluble barium sulphate turbidity. The resultant turbidity of the sample was then measured at 450 nm using a Hach spectrophotometer. The filtered APCE was used as a blank for calorimetric measurements.

2 g samples of the slag were used to analyze for the mineralogical phases before and after adsorption. The voltage and current at which the diffractometer was operated were 40 kV and 30 mA respectively. Spectra were acquired in the range of 2θ from 10° to 90° with a step size of 0.01° at the scanning speed of $1^\circ/\text{min}$.

A series of solutions containing different initial concentrations of sulphates and aluminium ions (in the range of 50 – 200 mg/L) will be prepared and employed for the batch adsorption studies at 25°C to check the applicability of the Langmuir and Freundlich adsorption isotherms under optimum conditions obtained.

The Langmuir adsorption is characterized by a homogeneous adsorption which assumes monolayer adsorption. The adsorption occurs at a finite number of definite localized sites that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites [10]. The Freundlich is a non-ideal and reversible adsorption isotherm. It can be applied multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [11]. The remaining concentration of sulphates and aluminium ions after adsorption will be measured and the amount of adsorption at equilibrium, $q_e(\text{mg/g})$ will be calculated by:

$$q_e = \left(\frac{(C_0 - C_e)V}{W} \right) \quad (1)$$

Where C_0 and C_e (mg/L) are the liquid-phase concentration of sulphates at initial and equilibrium, respectively, V (L) is the volume of the solution and W (g) is the mass of dry adsorbent used. The adsorption efficiency of aluminium can be calculated as:

$$\text{Adsorption percentage} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (2)$$

3. Results and discussions

3.1. Effect of pH concentration.

Figure .1 shows a comparison between the change of pH of the effluent using BOFS and GBFS.

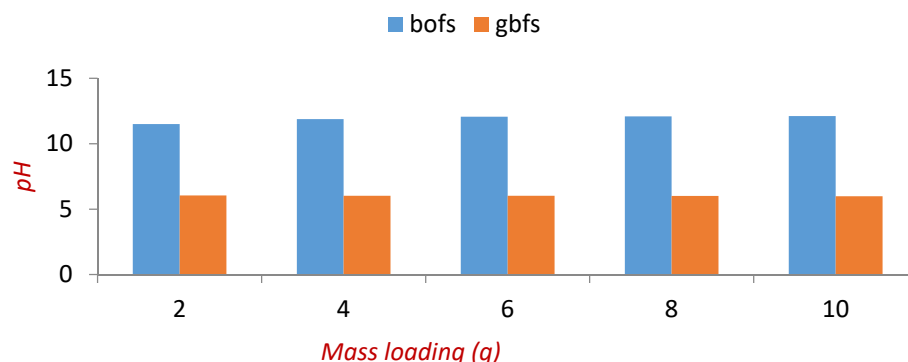


Figure 1. variation of pH with solid loading.

From Figure 1, it can be deduced that the pH of the effluent did not significantly change with increase in slag mass loading between 2-10 g/100 ml for both GBFS and BOFS. However, the final

pH obtained using BOFS (≈ 12) was almost double that obtained using GBFS (Figure 1), indicating that the neutralizing capacity of BOFS is much higher than that of GBFS. The amount of neutralizing bases (MgO+CaO) in BOFS was 47.7% as compared to 44.8% in GBFS, thus, the difference in neutralizing power is largely due to lower solubility of these bases in GBFS. Sulphates are mostly removed at an average pH of 12 [12], thus BOFS was chosen for further experiments.

3.2. Effect of solid loading

Figure 2 show the variation of % SO_4^{2-} removal with solid loading.

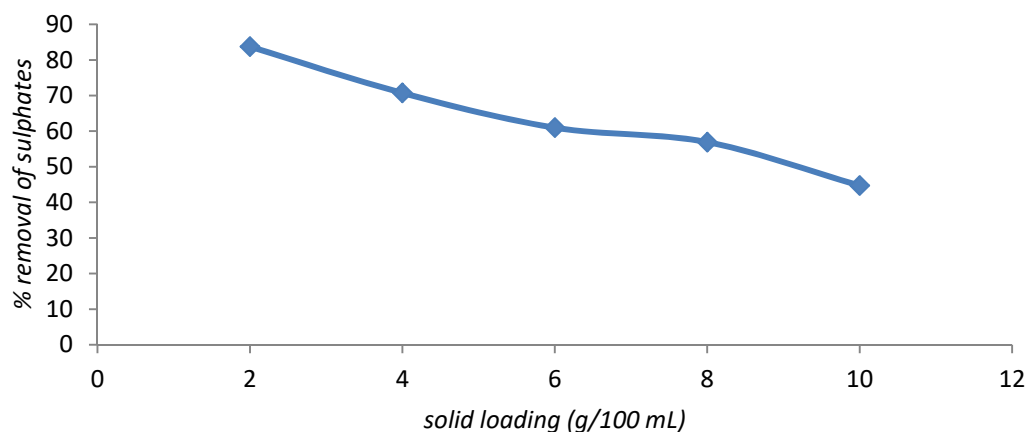


Figure 2. variation of % sulphates removal with solid loading.

The %sulphate removal decreased from 84% to 45% with increase in solid loading from 2 to 10 g/100 mL respectively. This was attributed to be largely due to decreased mass transfer with increasing solid loading [13] and a reduction in amount of slag suspended in solution at higher solid loading.

3.3. Effect of residence time

Figure. 3 shows the results obtained on the effect of residence time on sulphate removal.

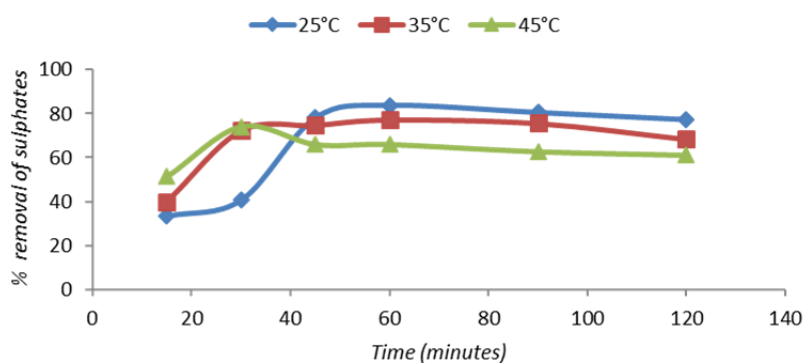


Figure 3. variation of % sulphates removal with time.

There was an increase in %sulphates removal with time up to 60 min. This is due to the increased contact time between the adsorbent and adsorbate. The %sulphates removal after 60 min decreased. The decrease can be due to the desorption. The highest removal was at 25°C and decreased with increasing temperature indicating the sorption process is endothermic.

3.4. Adsorption Isotherms

Figure 4: Langmuir isotherms and Figure 5: Freundlich isotherms shows the results that differs to each other. As deduced from the figures, the experimental data fitted better with Langmuir model for all temperatures with R^2 values greater than 0.98 (Figure 4). The Freundlich model also gave a satisfactory fit with R^2 values of greater than 0.965 [14]. The Langmuir parameters are shown in Table I. The R_L values at all temperatures were less than 1 (Table I), indicating that the adsorption was thermodynamically favourable.

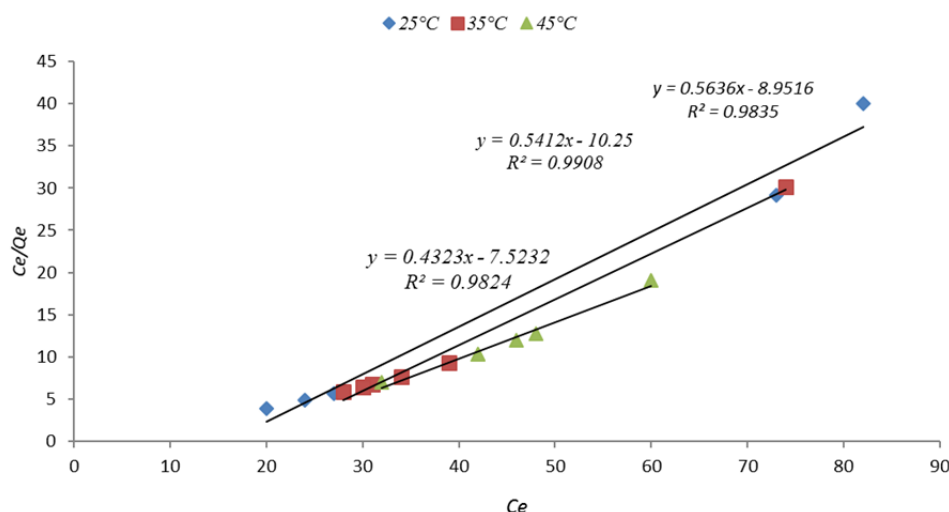


Figure 4. Langmuir isotherm.

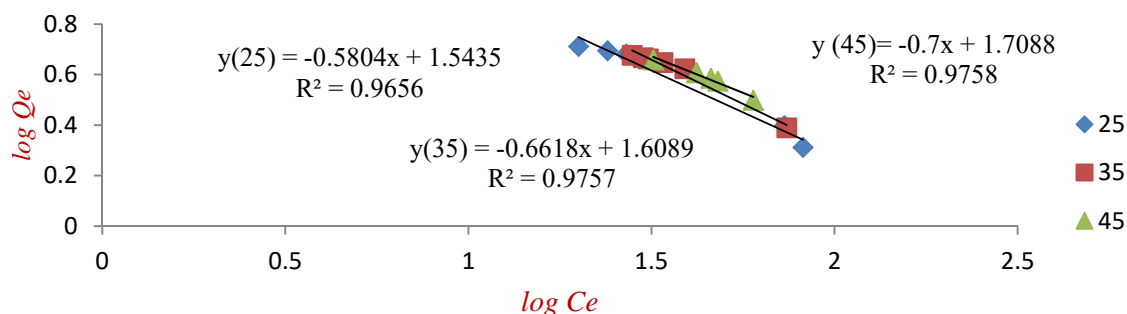


Figure 5. Freundlich isotherm.

Table 1. Langmuir isotherm parameters

T ($^{\circ}$ C)	b (L/g)	q_m (mg/g)	R^2	R_L
25	0.063	1.77	0.9835	0.114
35	0.053	1.85	0.9908	0.133
45	0.057	2.31	0.9824	0.124

3.5. Adsorption kinetics

The adsorption data best fitted the pseudo second order kinetics (Figure 6) and no acceptable fit was obtained for the pseudo first order kinetics at all temperatures.

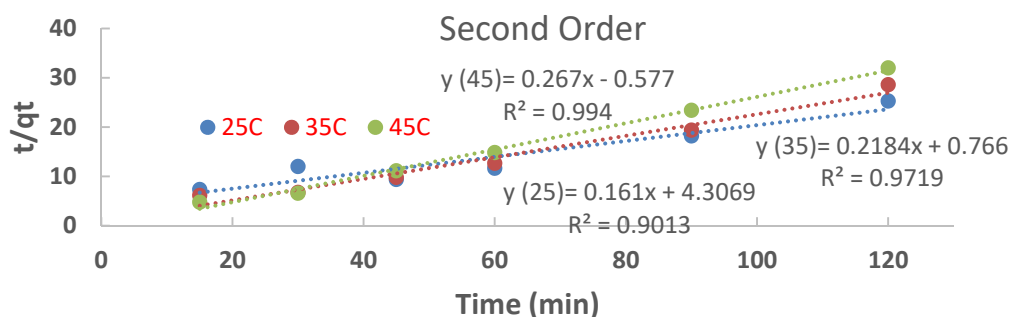


Figure 6. Pseudo second order kinetics.

The experimental data fitted the pseudo second order model well with correlation factors greater than 0.90. The accuracy indicates that the adsorption of sulphates onto slag can be described by the pseudo second order chemical reaction.

Table II shows the pseudo second order parameters

Table 2. Pseudo second order parameters

$T (^{\circ}C)$	B	$q_e \text{ calc}$	$q_e \text{ exp}$
25	0.955	6.21	4.95
35	0.986	4.58	4.65
45	0.997	3.74	3.85

The pseudo first order did not give a satisfactory fit. The q_e values for second order model were close to each other, increasing with an increase in temperature indicating that the experimental data is fitted well by the second order model. The q_e values for second order model were close to the experimental data indicating that the experimental data is fitted well by the second order model [1].

3.6. XRD analysis of BOFS

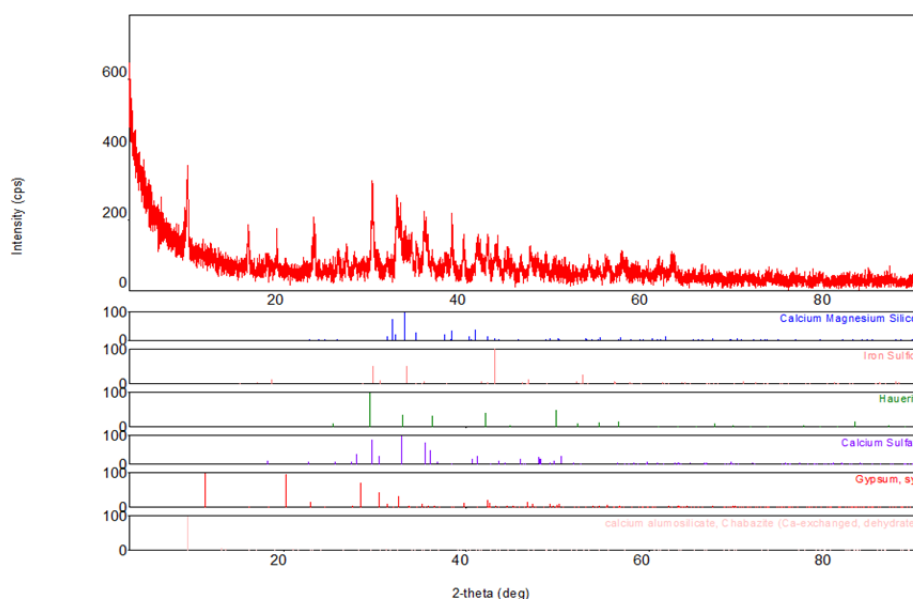


Figure 7. XRD for raw BOFS.

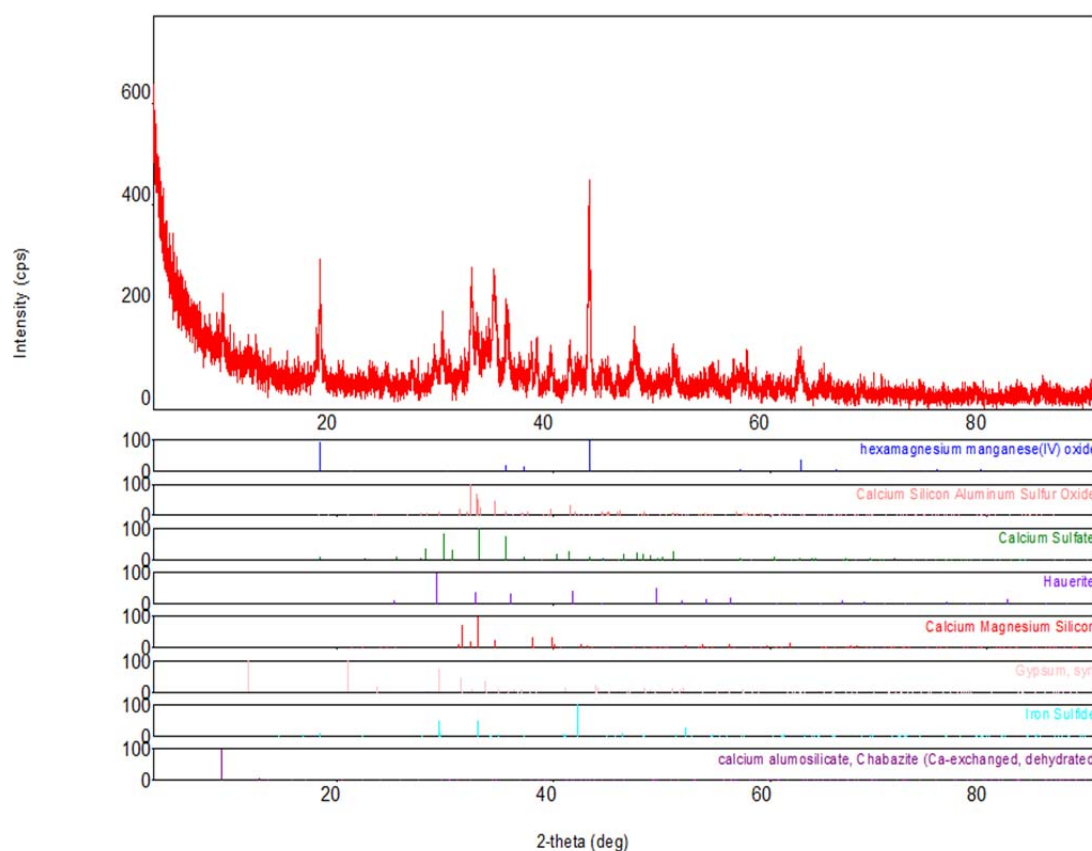


Figure 8. XRD for slag at 25°C.

Figures 7 and 8 shows the results obtained from the XRD analysis of the BOFS before sorption and after sorption. Comparing the two spectra it was observed that the sorption process was accompanied by the dissolution of the calcium aluminosilicate and gypsum phase as evidence by the disappearance of the peaks between 2θ angles between 0-20 deg. This indicates that Ca was the dominant neutralising ion as there was no significant dissolution of MgO. The new phases formed were hexamagnesium manganese (IV) oxide and calcium silicon aluminum sulphur oxide, indicating chemisorption was main sorption mechanism for removal of sulphates and other heavy metals in the effluent mainly Al and Mn.

4. Conclusions

Basic oxygen furnace slag can be used as an absorbent for sulphate removal. BOFS effectively raised the pH of the effluent from acidity to alkaline state. The final pH using a solid loading of 2g/100 ml of effluent was approximately 12 and 6 for BOFS and GBFS respectively. The higher pH obtained using BOFS enhanced the removal of sulphates from APCE. About 80% of the sulphates were removed within a residence time of 60 min using a BOFS solid loading of 2 g/100. The sulphate removal levels decreased with an increase in solid loading due to decreased mass transfer and a reduction in amount of slag suspended in solution. The adsorption mechanism was better modelled by the Langmuir isotherm. The sorption process was endothermic.

References

- [1] FU F, WANG Q 2011 Removal of heavy metal ions from wastewaters: A review *Journal of Environmental Management* **92** 407-418
- [2] Department of Water Affairs and Forestry 1996 South African Water Quality Standards Domestic Water Use 1 Second Edition
- [3] Gunatilake S K 2015 Methods of Removing Heavy Metals from Industrial Wastewater *Journal of Multidisciplinary Engineering Science Studies* **1** 12-18
- [4] Armarego WLF, Chai C 2013 "Chapter 4 - Purification of Organic Chemicals" in Purification of Laboratory Chemicals (Seventh Edition), ed. W.L.F.A. Chai, Butterworth-Heinemann, Boston 103-554
- [5] Beukes J P, Pienaar J J, Achmann G, Giesekke E W 2000 The reduction of hexavalent chromium by sulphite in wastewater - An explanation of the observed reactivity pattern, *Water SA* **26** (3) 393-395
- [6] Muharrem I, Olcay K 2017 An Overview of Adsorption Technique for Heavy Metal Removal from Water/Wastewater: A Critical Review *Int. J. Pure Appl. Sci.* **3**(2) 10-19
- [7] Kalmykova Y, Knutsson J, Strömvall A-M, Hargelius K 2010 Blast furnace sludge as sorbent material for multi-metal contaminated water *In Highway and Urban Environment, Proceedings of the 9th Highway and Urban Environment Symposium, Madrid, Spain*, 9-11 June, Rauch S, Morrison GM, Monzón A., Eds.; Springer: London, UK 2009 325-336
- [8] Johansson Westholm L 2010 The use of blast furnace slag for removal of phosphorus from wastewater in Sweden- A review. *Water* **2**(4) 826-837
- [9] Hedström A, Rastas L D R 2006 Methodological aspects of using blast furnace slag for waste-water phosphorus removal *J. Environ. Eng.* **132** 1431-1438
- [10] Kundu S, Gupta A K 2006 Arsenic Adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization *Chemical Engineering Journal* **122** 3289-3292
- [11] Adamson A.W, Gast A P 1997 Physical Chemistry of Surfaces. sixth edition, Wiley Interscience, New York
- [12] Madzivire G 2009 Removal of sulphates from south African mine water using coal fly ash, A thesis submitted in fulfillment of the requirements for the degree of Magister Scientiae in Chemistry. Department of Chemistry, University of the Western Cape
- [13] MacCarthy J, Nosrati A, Skinner W, Addai-Mensah J 2015 Acid leaching and rheological behaviour of a siliceous goethitic nickel laterite ore: Influence of particle size and temperature *Minerals Engineering* **77** 52-63
- [14] Gravelet-Blondin L R, Barclay S J, Carliell C M, Buckley CA 1997 Management of water resources in South Africa with respect to the textile industry *Water Science and Technology* **36**(2-3) 303-310